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54 Procedure for the direct hydroxylation of unsaturated carboxylic acids

57 Procedure for the direct hydroxylation of unsaturated carboxylic acids by  
converting in situ generated performic acid and/or peracetic acid.

The following information was obtained from the documents submitted by the  
applicant.

Description

The invention pertains to a procedure for the direct hydroxylation of unsaturated carboxylic acids via oxidation with hydrogen peroxide by means of intermediately generated epoxydized carboxylic acids and acid-catalyzed ring opening with the help of water.

These unsaturated carboxylic acids may be fatty acids. In this context the term fatty acids refers to fatty acid mixtures with varying contents of saturated and mono- and/or poly-unsaturated fatty acids whose composition is defined by the types of oils and fats used as starting substances as well as mono- and/or poly-unsaturated fatty acids isolated from such fatty acid mixtures.

Naturally occurring oils and fats (triglycerides) generally contain saturated as well as mono- and poly-unsaturated fatty acids. At times, even if this is rarely the case, fatty acids exhibit naturally occurring oils and also hydroxyl groups in their fatty acid residue. Among the oils used largely for industrial purposes, only castor oil possesses the property that its dominant fatty acid, that is ricinoleic acid, exhibits a double bond as well as a hydroxyl group per molecule.

Fatty acids per the above definition serve as a starting substance for the generation of a variety of technically important products. Fatty acids containing double bonds and/or hydroxyl groups are of special interest, as indicated for example in DE 41-25 031 C1, page 2, lines 19 to 26.

As hydroxylated fatty acids, aside from their OH-function, also exhibit unattached carboxylic groups, it is possible to obtain water-soluble products via the latter as well, which may for instance be of special interest in the case of varnish-binding agents and lubricants (adding lithates from hydroxy fatty acids.) As salts with amino alcohols, hydroxy fatty acids are the foundation for emulsifiers in textile processing agents as well as in cosmetic supplements.

Due to the presence of hydroxyl and carboxylic groups in the molecule of hydroxylated fatty acids, intermolecular esterification (poly-condensation)

between two and more molecules is possible. In this process, so-called estolides are generated which, depending on the hydroxy fatty acids' degree of condensation, still exhibit acid values between 50 and 100 and hydroxyl values between 100 and 200. Such estolides are interesting raw substances for the production of aqueous varnish resins, which may on one hand be processed to stove enamels in combination with urea resin and melamine resin and reticulated at room temperature as varnish film with polyisocyanates on the other hand. Estolides are also suitable anti-blocking agents for the shaping process of PVC and its copolymers.

Furthermore, hydroxy fatty acids, their alkalates and oligomer estolides are exceptionally well suited as corrosion inhibitors in lubricating oils and lubricating greases on a mineral oil basis.

In the manufacture of car tires, the use of hydroxy fatty acids in the form of their esters, ethers and salts leads to an improvement in tire control performance.

Among the oils gained from re-growing raw substances, sunflower oil's fatty acid mixtures and euphorbia lathyris oil, which are rich in oleic acid, are especially of interest.

Fatty acids with two or more hydroxyl groups per fatty acid molecule are known.

A hydroxylation procedure for the production of 9,10-dihydroxy stearic acid is known from US 2 443 280, which is performed by converting oleic acid with a mixture of hydrogen peroxide and acetic acid as well as catalytic quantities of a strong acid such as sulfuric acid. The resulting hydroxy-acetoxy-stearic acid is subsequently processed to 9,10-dihydroxy stearic acid by means of saponification with the subsequent decomposition.

DE 41 25 031 describes the hydroxylation of epoxydized fatty acid methyl ester and subsequent decomposition to hydroxy fatty acid. Hydroxylation takes place by converting epoxydized fatty acid methyl ester with water in the presence of acid-activated alumina, silicates or activated carbons.

Further, T.M. Luong, H. Schrifman and D. Swern describe the production of threo-1,2-glycols in J. Am. Oil Chem. Soc. 44, 316-320 (1967), starting with certain water-insoluble mono-unsaturated fatty acids by means of intermediary epoxides via in situ hydration and inversion with the help of a hydrogen peroxide-tungstic acid-oxidation system. Thereby, the starting product oleic acid was emulsified in water with the help of an emulsifier and/or the hydrogen peroxide-tungstic acid-oxidation system was conditioned 20 minutes to 5 hours prior to use.

EP 0 025 940 B1 describes the production of dihydroxy-stearic acid, starting with oleic acid, whereby 1 mole oleic acid and 4 moles formic acid are used and 1.1 mole of the oxidation substance hydrogen peroxide is added to this mixture at 50°C during the course of 1 hour. Within another hour, the reaction mixture converts completely. The product of the conversion must be saponified with sodium hydroxide and subsequently decomposed with concentrated hydrochloric acid, whereby raw dihydroxy-stearic acid is obtained at a yield of approximately 95%. The raw acid can then be transformed into a pure product by means of crystallizing ethyl acerate.

The purpose of the invention is to provide a procedure for the production of hydroxylated carboxylic acids, which exhibit two or more centrally located hydroxyl groups per molecule, and which is performed in an economical and non-polluting manner. The purpose of the invention is especially to provide hydroxylated fatty acids with two or more hydroxyl groups, which are usually in the area of C-atoms 9 to 16. To solve this task, the procedure according to the main claim is recommended. The sub-claims contain preferred development examples of the procedure.

Considering the state of technology, it is entirely surprising that it is possible to gain a good yield of hydroxy fatty acids directly, starting with fatty acid mixtures of varying high contents of mono- and poly-unsaturated fatty acids by means of appropriate procedure performance via intermediately generated epoxydized fatty acids and acid-catalyzed ring opening with the help of water.

The acid-catalyzed ring opening of the intermediately generated epoxydized fatty acids' oxiran ring according to the invention is performed practically completely. The reaction requires only small catalyst quantities and progresses smoothly without the necessity of extensive post-processing such as described in EP 0 025 940 B1, for example. This is also the reason why the invention's procedure is considered particularly non-polluting, as practically no disposal problems arise.

The yield of pure polyhydroxy fatty acids, as it pertains to the quantity of the fatty acids', respectively fatty acid mixtures', en-acids used, amounts to approximately 70% to 80%, whereby the deviation from the theoretical yield can be explained with the generation of estolides.

The advantages of the procedure according to the invention compared to the above known procedures are specifically:

1. that polyhydroxy fatty acids are obtained directly in a one-step procedure with a high yield of approximately 70% to 80%, and that
2. the required quantity of acid (formic acid and/or acetic acid) is considerably lower and the reaction product's process can therefore be substantially simplified and designed more gently.

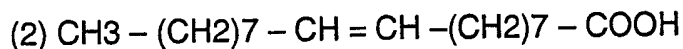
These advantages by far offset the disadvantage of a slightly longer reaction time than that with EP 0 025 940 B1.

In order to perform the procedure, mono- and/or poly-unsaturated carboxylic acids, preferably fatty acid mixtures with varying contents of mono- and poly-unsaturated fatty acids, whose composition is defined by the types of starting oils and fats on which these fatty acid mixtures are based, are converted with an oxidizing agent consisting of a mixture of hydrogen peroxide (35% to 98%, preferably 50%) and formic acid and/or acetic acid as an organic acid (80% to 100%, preferably 85%) at temperatures of 25°C to 90°C, preferably 65°C to 80°C. As it pertains to the quantity of fatty acid used, hydrogen peroxide (calculated as 100% agent) is used in a quantity of 1.05 to 1.3 mole,

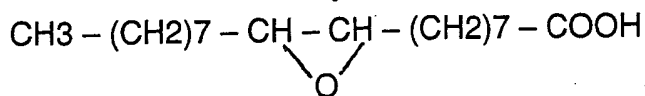
preferably approximately 1.3 mole per mole double bond. The quantity of formic acid and/or acetic acid (calculated as 100% agent) in the reaction mixture amounts to 0.3 to 1.0 mole, preferably 0.4 mole per mole double bond. Formic acid and/or acetic acid and hydrogen peroxide are dispersed preferably over the entire reaction time in 6 to 8 portions, added one after the other, in order to be able to better control the hydroxylation process taking place exothermally.

The reaction heat generated during the process is discharged via intensive water cooling. On one hand, the reaction's progress is monitored by determining the iodine value, which decreases due to the generation of epoxydized fatty acids, and by determining the contents of oxiran, which indicates that intermediately generated epoxydized fatty acids are being converted into the respective hydroxyl compounds by means of ring opening, on the other hand. The process is considered complete as soon as the iodine value reaches a value of approximately 2 in the reaction mixture. Experience has shown that at this point in time the epoxide groups generated intermediately as a precursor to hydroxylation are practically completely disintegrated. The entire reaction time takes between 5 and 12 hours. During the hydroxylation of unsaturated carboxylic acids, the oxidizing agent is the peracid resulting from the conversion of hydrogen peroxide and formic acid and/or acetic acid. This peracid reacts with the unsaturated carboxylic acids' double bonds, whereby epoxydized carboxylic acids are generated intermediately. The latter possess very limited stability in their acidic medium, as the acid (formic acid and/or acetic acid) acts on the epoxide ring and opens it. The water existing in the reaction mixture, which was created by disintegrated hydrogen peroxide, is accumulated in this process, forming vicinal hydroxyl groups. Due to the way the procedure is performed, the generation of polyol formates is largely suppressed. Hydroxylation of unsaturated fatty acid can be illustrated by means of the following reaction diagram:

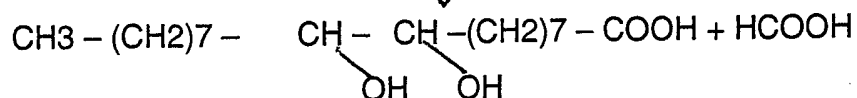
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Oxidizing agent



Water



The following examples explain the preferred design development of the invention.

## Example 1

### Hydroxylated Fatty Acid From Turnip Oil

2500g Fatty acid from turnip oil with an iodine value of 113 were placed into a 6-liter reaction container equipped with an agitator, thermometer and drip funnel and brought to a reaction temperature of 70°C by means of heating a water bath. Subsequently, 1010g hydrogen peroxide (50%) and 225g formic acid (85%) in 7 roughly identical portions were added via the drip funnel one after another, distributed over the entire reaction time of 11.5 hours, while stirring intensely. The reaction heat generated during the process was discharged via a tempered and suitably sized water bath. The hydroxylation reaction's progress was monitored by determining the iodine value and oxiran contents. After reaching an iodine value of approximately 2 in the reaction mixture, the process was interrupted. At this point in time, the content of oxiran was already below 0.1%. After processing the reaction mixture by clarifying the sour water, repeated

washing and drying, the classification values for hydroxylated fatty acid from turnip oil, summarized in the following table, were determined.

#### Examples 2-9

#### Hydroxylated Fatty Acids From Different Oils

As in the procedure in example 1, the fatty acids from different oils were hydroxylated, whereby the hydrogen peroxide and formic acid to be used in each individual case were reduced to the respective iodine value of the fatty acid used. The classification values of the hydroxy fatty acids thereby generated, are listed in the following table.



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TABLE : Classification values of hydroxylated fatty acids on native oil basis

| Example | Type of fatty acid | SZ  | VZ  | JZ   | OHZ | Oxiran % | Viscosity<br>° C./mPa.s | Gardner<br>Color |
|---------|--------------------|-----|-----|------|-----|----------|-------------------------|------------------|
| 1       | Turnip oil         | 138 | 216 | 6.5  | 219 | 0.05     | 25/ 13,000              | 5                |
| 2       | Euphorbia lath.    | 138 | 222 | 8.2  | 232 | 0.19     | 40/ 1,500               | 5                |
| 3       | Soy oil            | 156 | 210 | 15.3 | 255 | 0.55     | 25/ 23,200              | 4 - 5            |
| 4       | Sunflower oil      | 140 | 212 | 1.0  | 222 | 0.33     | 40/ 3,100               | 2                |
| 5       | Tall oil           | 127 | 206 | 6.7  | 257 | 0.25     | 25/ 52,300              | 4                |
| 6       | Linseed oil        | 137 | 219 | 11.4 | 237 | 0.12     | 40/ 32,200              | 9 - 10           |
| 7       | Fish oil           | 142 | 202 | 6.4  | 204 | 0.08     | 40/ 920                 | 3 - 4            |
| 8       | Came line oil      | 136 | 211 | 7.0  | 262 | 0.16     | 40/ 12,100              | 3 - 4            |
| 9       | Olive oil          | 148 | 214 | 1.4  | 160 | 0.06     | 40/ 900                 | 3 - 4            |

SZ :        Acid value  
VZ :        Saponification value  
JZ :        Iodine value  
OHZ :      Hydroxyl value

### Patent claims

1. Procedure for the direct hydroxylation of unsaturated carboxylic acids by converting performic acid generated in situ and/or peracetic acid as organic acid at an increased temperature of 25°C to 90°C, whereby formic acid and/or acetic acid are used in quantities of 0.3 to 1.0 mole per mole double bond of unsaturated carboxylic acid, and hydrogen peroxide is employed at a concentration weighting of 35% to 98%.

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2. Procedure according to claim 1, characterized in that performic acid is used as organic peracid for oxidation.
3. Procedure according to one or more of the aforementioned claims, characterized in that the oxidation of unsaturated carboxylic acids is performed at temperatures of 65°C to 80°C.
4. Procedure according to one or more of the aforementioned claims, characterized in that hydrogen peroxide and organic acid are added to carboxylic acid, which is to be oxidized, in several portions, dispersed over the reaction's entire time period.
5. Procedure according to one or more of the aforementioned claims, characterized in that as a starting substance fatty acid mixtures of vegetable and/or animal oils and fats and/or mono- and/or poly-unsaturated fatty acids isolated from such fatty acid mixtures are used.
6. Procedure according to one or more of the aforementioned claims, characterized in that other olefinic aliphatic carboxylic acids are used as a starting substance.
7. Procedure according to one or more of the aforementioned claims, characterized in that hydrogen peroxide is used at a molar surplus of 5% to 30%, relative to the contents of double bonds.